

Immobilization of Nuclear Waste Graphite Using the SiC Synthesis Route - 11484

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ABSTRACT

Graphite has been used to a great extent throughout the history of the nuclear reactor, primarily as moderator material, neutron reflector material and structural material in the reactor core. As a result of both its natural properties and change in properties post irradiation, it is a particularly difficult material to dispose of without correct immobilization with an aim to improve the mechanical properties of the waste form. A novel method for the immobilization of the graphite using the silicon carbide synthesis route is considered. Mechanochemical alloying presents a unique opportunity in the synthesis of silicon carbide, by mechanically milling graphite and silicon powders at low temperatures followed by a low temperature sintering stage, resulting in a streamlined easily scalable process suitable for dealing with potentially volatile irradiated materials. The synthesis process itself and as a potential waste immobilization technique and direct use of silicon carbide synthesized as a reinforcing filler for concrete or cementitious wastefoms (in the context of irradiated graphite waste) is examined.

INTRODUCTION

The safe and energy efficient processing and disposal of nuclear wastes are highly contentious issues, which are under the constant scrutiny of both public opinion and international regulatory bodies. The wastes often contain radionuclides of long half-lives which in the case of inappropriate waste forms being disposed, can result in the contamination of the biosphere leading to damage to the organisms inhabiting these areas for up to millions of years. Many materials upon removal from nuclear reactors are unsuitable for direct disposal, either as a result of their natural properties or the change in properties post irradiation. In addition to the inevitable inventory of radionuclides amassed during irradiation within the reactor core what remains is a material which is difficult to dispose of effectively such that its isolation from the environment for the long term future can be guaranteed.

Graphite is one such material and has been extensively used in the nuclear industry since the very first experimental reactors were put into service[1]. Large quantities of graphite have been used worldwide, with the greatest stockpiles of irradiated graphite being the United Kingdom, Russia, USA and France, in order of decreasing amounts stockpiled[2]. The most significant proportion of the stockpiled graphite is a result of the graphite used as moderator material in Advanced Gas Reactors (AGR) and MAGNOX reactors in the UK, and RBMK and Bilibino reactors in Russia [3]. It is estimated that there is a total of 81,000 tons of graphite waste to be dealt with in the UK in decommissioning [4]. Although the majority of the graphite is used as moderator material, where it scatters energetic neutrons such that their energy is reduced to the thermal level, it is also used as reflector material and a structural material in the fuel matrix. Graphite is chosen primarily because of its relatively low absorption cross-section and high scattering cross-section for neutrons, hence negligibly decreasing the free neutron population within the reactor core.

Within the core, the graphite is subject to a high flux of high-energy neutron bombardment. Over time this results in the irradiation of the graphite and a slow buildup of various species of radionuclides in its inventory. The most populous radionuclides found in the irradiated graphite are C-14, H-3 and Cl-36 [4, 5]. These are commonly generated from the following routes: (i) N-14(n,p)C-14, (ii) C-13(n, γ)C-14, (iii) O-12(n, α)C-14, (iv) Li-6(n,He-4)H-3 [7] and (v) Cl-35(n, γ)Cl-36. Of these generation routes, all but route (ii) are due to contaminants and not the graphite itself, however all can be dangerous to organisms if these radionuclides are released into the environment. It is important to note however that the exact radionuclide inventory varies from sample to sample depending on reactor type, manufacturing processes undergone, period within reactor and the fuel being burnt in the core. It is reported that the dose rate from irradiated graphite on average requires 80 years after removal from the core to level out to a value of one magnitude greater than the background dose rate[2].

Upon retrieval from the reactor it is seen that the graphite is difficult to remove, as its (mechanical) properties have changed as a result of the irradiation. Not only does this result in a poorer waste form, but graphite's initial properties are inappropriate for disposal as well, hence the resultant waste form is especially inadequate. During irradiation the most significant changes are mechanical, such as the decrease in strength, additional internal stresses and embrittlement [5]. However, secondary effects are also present such as cracking and changes in the heat dissipation character within material. These factors all contribute to the wastefrom being mechanically weak. Over time, due to the intense neutron irradiation there is significant disruption on the atomic scale where the high-energy neutrons interact with the regular and consistent crystalline structure and cause dislocations, stacking faults, interstitials, and other energetically unfavorable configurations. This results in a buildup of potential energy known as Wigner energy, which under the correct conditions may be released resulting in a local temperature increase, which literature suggests can be up to 2.7 kJ/g [8]. However, to overcome this, an annealing stage maybe added to release the potential energy in a controlled manner. It is also important to note that this build up of Wigner energy is only present in older reactors which operate with the graphite at near or just above ambient temperature, hence the buildup is not so significant in newer reactors where the graphite is exposed to is much higher temperatures[5]. The graphite used in nuclear application as a monolith exhibits an initial pore density of ~ 20 % [9,10], this is unfavourable when considering disposal and the minimization of radionuclide leaching. In fact, non-porous graphite-glass composite materials have been developed by Fachinger et al. [11].

Immobilization of graphite waste has been considered, such that upon successful immobilization into a suitable matrix the resultant product is durable and suitable for long-term disposal in that the possibility of radionuclides escaping from the waste material is minimized. A variety of techniques and host matrices have been researched, including self sustaining reactions in the C-Al-TiO₂ [12,13],

A significant feature of all of these immobilization techniques is that they all involve at least one high temperature stage. Even in a non-nuclear waste context, this is undesirable, however an alternative is considered, whereby the processing occurs at ambient temperatures. Mechanochemical alloying has been chosen to be considered as a potential technique to synthesis silicon carbide using graphite and silicon powder precursors. Mechanochemical alloying is a two-stage process, where the precursors are initially milled in a planetary mill for a number of hours; this is followed by a low temperature sintering stage in an argon atmosphere. Mechanical activation has been proved as an effective means to decreasing sintering reaction temperatures in waste immobilization [14].

Mechanical alloying has been cited by a number of publications as an effective technique to synthesize nanocrystalline carbides [15,16]. This technique requires a high-energy ball mill, which has mounted grinding bowls that rotate in a planetary fashion around a central axis of rotation. Within the grinding bowls there is milling media in the form of spherical balls, which are free to move within the containers. As the speed of rotation of the platform increases, upon which the bowls are fixed (but are free to rotate themselves, allowing the planetary motion), the speed of the bowls also increases and their angular velocity is much greater than that of the platform. The motion of the milling media varies for different angular velocities, however the intended behaviour is the case where the balls maintain contact with the side walls of the cavity of the bowl and travel in a circular motion, until a point at which they lose contact with the wall and fall away inevitably colliding with either another part of the inner wall of the bowl or another milling ball. It is at this interface where the feedstock powders maybe trapped and experience large forces during the collision. The rapid motion of the balls and somewhat erratic motion during collisions helps in mixing the particles, however it is at the interface during collisions where a more complicated process takes place. Initially the particles caught at the interface are joined together whilst they are soft however over time they become work hardened as there is flattening and subsequent collisions cause fracturing of the powder particles[17]. In addition, a large quantity of heat is generated locally at the point of collision, which results in the rewelding of the fractured powder particles. Over time the powder particles develop a layered structured with an intimate stacking of precursor material, with greater milling periods this becomes more complex and the microstructure of the particles also changes, the crystallinity of the material reduces. This results in the dramatic reduction of the migration distances between atoms, and under the conditions, new material is synthesized.

Often, depending on the milling parameters such as milling period, speed of rotation of grinding bowl and feedstock to milling balls to container volume ratios, there is some unreacted precursor remaining which requires extra processing to maximize the yield of the intended synthesis product. Hence, a secondary processing stage is introduced which is a low temperature sintering stage under an argon atmosphere. Although solid state sintering is often considered to be a complete and comprehensive process in its own right, in this case lower temperatures are required as a lot of the synthesis has already occurred and the remaining precursor is mechanically activated in that it is well mixed and the crystalline structure is somewhat damaged increasing the ease of migration with the aim of product synthesis, as exploited by Batyukhova et al. [13]. The advantage of pairing these two processes together is the way that they complement each other. The initial mechanical alloying ensures a very fine average particle size and a very high level of homogeneity of the total sample. This is beneficial, as already discussed the migration distances for the atoms are dramatically decreased, in that the temperatures required for additional sintering process are far reduced. This reduction in temperature is beneficial from both an efficiency and a nuclear waste context viewpoint.

The intended synthesis product is silicon carbide. Based on published literature concerning the reliability and effectiveness of the mechanical alloying technique, not only in general but also in the specific synthesis of silicon carbide [15,18,19], this two stage technique for the specified application is promising. The synthesis product itself was chosen, and the processing stages specifically designed, because of the advantageous mechanical properties of silicon carbides. It is a particularly resistant and stable material especially to oxidation resistance and with high strength retention over a large temperature range[20]. Furthermore, its good thermal properties, extreme hardness, low porosity, chemical durability and high resistance to corrosion attacks by leachants indicate that it is a very effective waste disposal material[21].

Another option for silicon carbide produced is its as reinforcing filler for waste containers and cementitious wastefoms as in Figure 1.

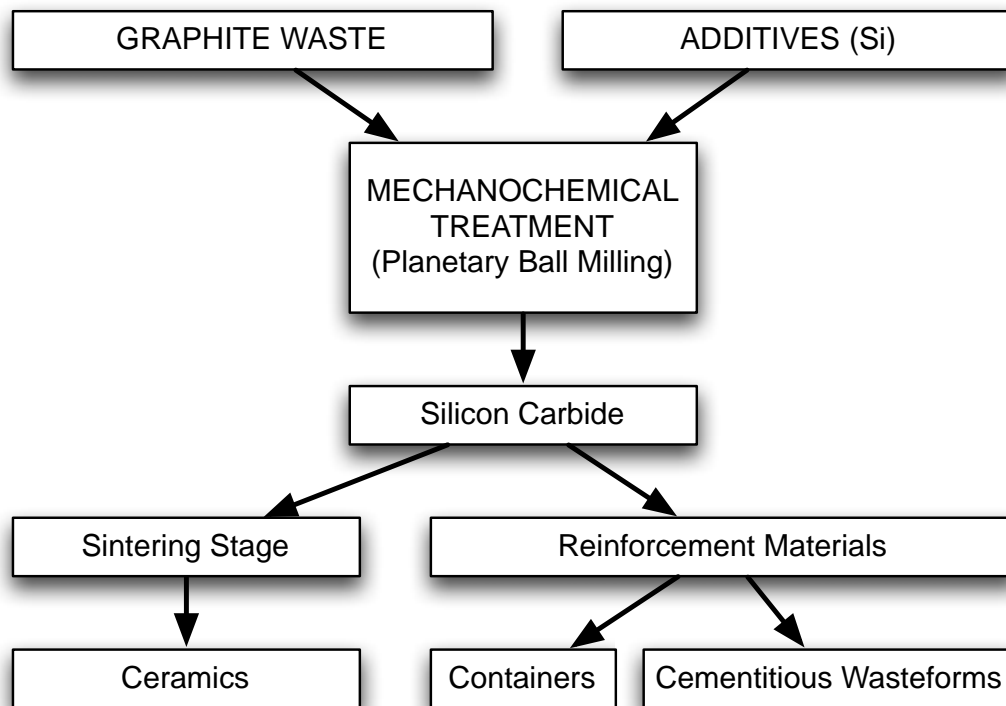


Figure 1. Schematic showing the processing stages for various applications of the technique specific to irradiated graphite waste.

Silicon carbide is commonly cited in literature to be a good reinforcement material for cements and castables, and this would be an ideal reuse for the synthesized silicon carbide. However, the activity associated with the synthesis product would be far too great for any civil application. However, there are certain applications within the nuclear waste management sector itself where the silicon carbide maybe able to be incorporated into cements. Graphite itself is very difficult to incorporate into cements, however in the form of the synthesized silicon carbide it is possible to incorporate into the cements used in the manufacture of waste disposal containers. Waste disposal containers often use large quantities of cement which can be strengthened through the incorporation of silicon carbide and also this reduces the quantity of the graphite to be disposed of substantially. Cement is involved in three major aspects of waste disposal, (i) in encapsulating waste in disposal waste drums, (ii) in the voids in the walls of the overpack of the drums, and (iii) in the vault backfill. Hence these large quantities of cement maybe ideal for not just reusing some immobilized graphite and avoiding construction of greater storage facilities for the waste but also improving the mechanical properties of the cement used throughout these facilities.

EXPERIMENTAL

Graphite and silicon powders each of 99% assay and of -325 mesh (particle sizes of less than 44 μm) were used. Precursors were measured such that the total weight sum of the powders was 7.0000 ± 0.0005 g. The specific powders were chosen because of their common availability and low cost. Samples were prepared in various molar ratios of silicon to carbon, however still maintaining the total mass of 7 g per sample, hence maintaining the sample to milling ball ratio. Sample #1, #2 & #3 had silicon to carbon molar compositions of 1:1, 2:3 and 1:2 respectively.

The powders were milled in a Fritsch grinding bowl, of capacity 45 ml. It was anticipated that upon synthesis of silicon carbide, lengthy periods of subsequent milling would result in abrasion of the inside of the grinding bowl, hence a milling bowl constructed of zirconium oxide was chosen to avoid any abrasion and subsequent contamination of the sample. Eight milling balls of the same zirconia were chosen as the milling media. The planetary mill used was a Fritsch Planetary micro mill pulverisette 7. An airtight seal for the grinding bowl was ensured and only then did milling commence. The ratio of the angular velocity of the rotating platform and that of the grinding bowl was calculated to be -1 ± 1.495 and the % critical speed, CS, to be 80.2 % CS, this was kept the same for all samples. However what did differ between the samples are the milling profiles, it was not possible to keep this the same for all samples.

Initially sample #1 was milled for a cumulative total of 40 hours, however this was not continuous and the milling profile was erratic and long periods of continuous milling were rare. At 2, 10, 20 and 40 hours of milling, sample #1 was subjected to XRD analysis. Subsequent samples #2 and #3 were milled and analysed by XRD after the total of 40 hours.

After milling a sample completely a rigorous protocol was in place to ensure that all salvageable sample was removed from the grinding bowl and it was cleaned. This was achieved by wet milling silicon carbide for a period of 10 minutes. This resulted in the removal of the thin but stubborn to remove sediment, left by the 40 hours of milling, from the inner surface of the grinding bowl and the milling balls. This protocol was used before commencing milling any unmilled sample.

The second stage of processing, the low temperature synthesis, was carried out for the stoichiometric sample #1. However the effect of sintering at different temperatures was measured by firing at two different temperatures quantifying the differences in the samples. Firing was conducted at 600 and 900 °C. The heating profile began at room temperature and increased at a rate of $2 \text{ }^\circ\text{C s}^{-1}$ until the target was achieved, at which it remained constant for 90 minutes, followed by cooling back to room temperature at the same rate as the increase. Samples were inserted into furnaces not as pellets, but in crucibles and an atmosphere of argon was present throughout the firing process.

Experiments on silicon carbide as a filler material will be carried out later once the ideal milling process has been established.

CHARACTERIZATION TECHNIQUES

XRD

X-Ray Diffraction (XRD) was chosen as a technique to document the change in the content of materials of the sample, hence checking for the synthesis of new products and to note any contamination of the sample from the milling and firing process. In addition, as the technique relies on crystalline samples, it also checks for amorphisation of the sample. In the case where the crystal structure changes significantly from crystalline to amorphous, this is evident in the XRD analysis. It is an ideal technique for such an application as it is non destructive, useful in a process where samples sizes are relatively small. Analysis was performed using a Philips PW1710 reflection diffractometer utilizing cobalt radiation. Sample #1 was analyzed at particular intervals during the milling period totaling 40 hours, to assess the effect of milling period upon the change in the sample. In addition analysis was conducted on samples #1-3 after the total milling period and after the sintering stages and compared.

SEM

Scanning Electron Microscopy (SEM) was considered as a technique in achieving high-resolution images of the microstructure of the samples post milling, not only was the particle size investigated but also the levels of agglomeration within the sample. In addition, the EDS (Energy Dispersive Spectroscopy) made available a further check against contaminants within the sample. Although SEM is a destructive method of analysis it was noted that the SEM sample size to overall sample size was relatively low and hence the detriment to the sample was relatively low. Furthermore, all SEM analysis is performed post milling process. Hence as the change in the sample size only has synthesis implications during the milling process. For example if the sample was tampered with part way through the forty hour milling period and the sample size changed significantly it would have consequences on the sample size to ball to milling volume ratio and this would affect the force and the collision mechanics hence altering at least the rate of synthesis if not other properties of the synthesis product as well. SEM analysis was performed on a FEI Inspect F microscope capable of resolutions on the nanoscale. Samples were sonicated for 1 hour in a solution of isopropyl alcohol at a frequency of 35 kHz, this was done to break down inevitable agglomerations of particles.

DTA

Differential thermal analysis (DTA) is a technique based on the principle of subjecting a sample to a range of temperatures, and recording the change in temperature of the sample with respect to a known sample, which is stable over this range. Hence, thermally activated processes that occur at specific temperatures within the range the temperature is being varied may be identified and additional knowledge concerning the sample and its behavior attained. It is documented that silicon carbide when heated in an atmosphere of air undergoes particular processes, hence DTA is a useful technique to check for the presence of the synthesis product. Three samples were analyzed : (i) Sample #1 post milling with no sintering stage, (ii) Sample #1 after a 600 °C firing, and (iii) Sample #1 after a 900 °C firing. Analysis was performed in 60 mm³ crucibles heated from room temperature to a final temperature of 1200 °C at a rate of 10 °Cmin⁻¹ all in an atmosphere of air. DTA was chosen as it was a more definitive and conclusive technique in the aim to check for silicon carbide, as it did not rely on the sample being crystalline and was far more precise than EDS.

RESULTS

XRD

Traces were taken for Sample #1 at various intervals during milling, as shown in Fig. 1.

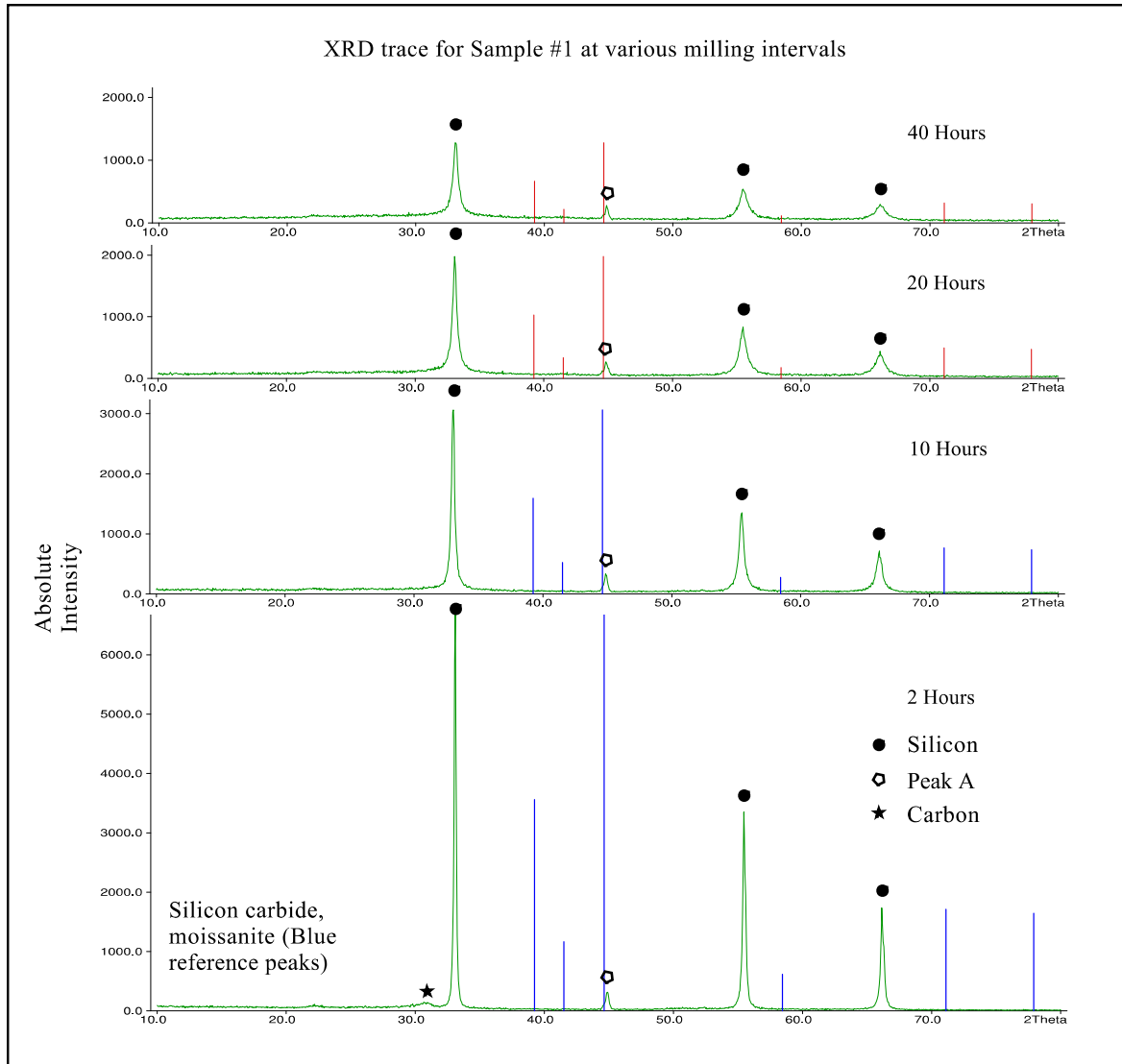


Figure 2. Shows the evolution of the XRD trace obtained for Sample #1 at various elapsed milling hours.

XRD analysis was also carried out for samples #1-3 after a cumulative total of 40 hours of milling each and compared. It was noted that the same signature trace was present as in Figure 2. Very little difference was present between these samples which only differed in their composition and nothing else; the milling process was the same. The same silicon peaks were present with the additional peak A with the same intensity.

The same analysis was conducted on sample #1 after it had been fired at 600 °C and 900 °C (post milling), and these were compared with the trace for sample #1 with milling but no firing stage. It was found that the sample fired to

600 °C maintained a signature trace almost identical to that of the unmilled sample, whereas that of the sample fired to 900 °C exhibited more intense silicon peaks and a slightly more intense silicon carbide peak.

SEM

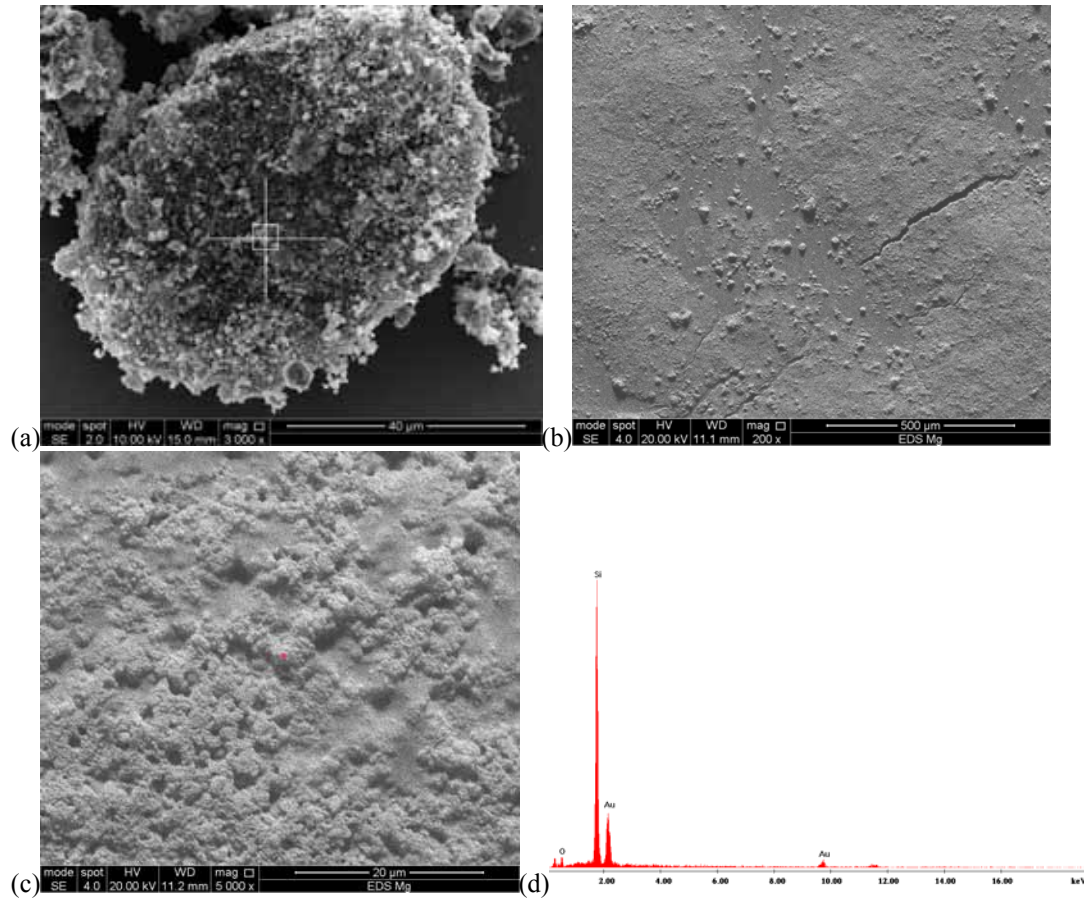
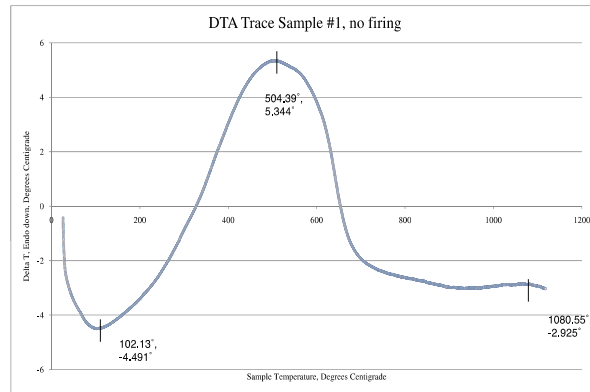


Figure 3. Showing (a) an average agglomerate from sample #1 without sonication, (b) low magnification image of same sample post sonication, (c) high magnification image of the same sample and point of EDS analysis, and (d) the EDS data obtained at the location marked in (c).

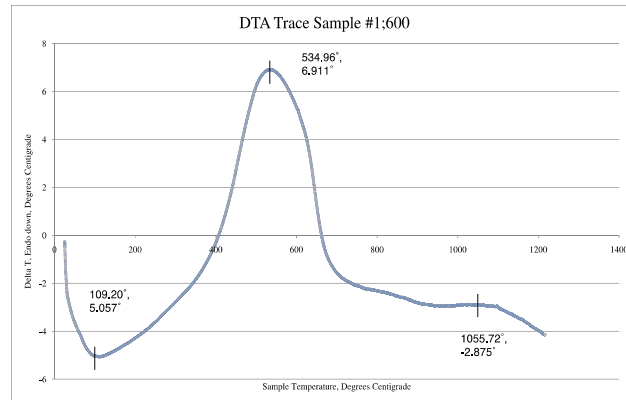
DTA

DTA was performed on Sample #1 with no sintering, sintering at 600 °C and sintering at 900 °C, results obtained are shown in Figure 4.

(a)



(b)



(c)

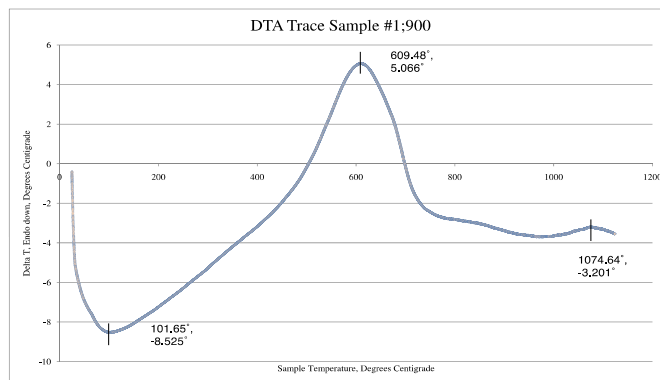


Figure 4. DTA curves for (a) Sample #1 with no sintering stage, (b) Sample #1 sintered at 600 °C and (c) Sample #1 sintered at 900 °C. Where in each the X axis is the Sample temperature in degrees centigrade and the Y axis is Delta T also in degrees centigrade.

DISCUSSION

The XRD analysis of sample #1 shown in Figure 2, indicates that large quantities of silicon and carbon are present throughout the milling cycle of the 40 hours. However there is a small weak peak, labeled Peak A in the figure, which lies in the same position as that of the prominent peak for silicon carbide. Peak characterization software identifies this peak with a closest match of moissanite silicon carbide, however also associated with this peak are multiple smaller peaks; the absence of these peaks maybe attributed to the small size of the predominant peak and hence it may be assumed that these peaks are lost in the signal noise. However it may be that the synthesized silicon maybe in an amorphous state as well, hence undetectable by XRD. This peak ties in well with results obtained in the literature[19]. However the peak is of low intensity and hence its characterization is not conclusive, however combined with the literature it is a good marker that silicon carbide has been synthesized.

It is interesting also to consider the change in the peaks of the silicon and carbon as well, as this informs us about what is occurring to the sample for the duration of the milling. XRD traces obtained of the silicon and carbon before milling indicate multiple carbon peaks, however their presence is undetected albeit for a small carbon after 2 hours of milling. Hence after 2-10 hours of milling the carbon peaks are not present on the XRD trace. The silicon peaks also change in their intensity as a function of the milling period, with each subsequent XRD trace the intensity of the silicon peaks all relative to Peak A decrease in intensity. Both of these effects can be attributed to the amorphisation of the precursors within the grinding bowl, hence reducing their detection by x-ray diffraction. This amorphisation of precursors during the mechanical alloying process and within the field of milling in general is well commented upon by literature [22,23,24]. Hence it is a sound conclusion to draw that the carbon is amorphised and that with milling time increasing the proportion of amorphous silicon.

XRD analysis indicated the negligible effect which the molar ratio of silicon to graphite powder had upon the milled sample. It is clear that the impact was very little if any at all as the traces all have the same signature shape and the same intensities of peaks. However conclusions may not be drawn conclusively that the different ratios of powders did not have an effect on the sample and synthesis product. It maybe that a small amount of silicon carbide was synthesized such that the quantities of any precursor excesses did not manifest on the XRD analysis, however in further work where greater yields of silicon carbide are obtained the molar ratio of silicon to graphite may be influential. Further, XRD analysis showed the effect that the firing stage has upon the sample and the difference with firing temperature. It seems as though the 600 °C firing stage has little effect on the sample and the 900 °C firing stage has more effect. The sample fired to 600°C showed a very similar trace, to the unfired sample, implying the firing stage did not affect the crystal structure greatly. The latter increases the proportion of the silicon, which is crystalline, indicated by the higher intensity silicon peaks for this sample, however the supposed silicon carbide peak is not significantly greater in intensity in comparison to the other trace to deduce anything conclusively. It can be said that the sintering stage is either not conducted at high enough temperatures or that the dwell period was not long enough to crystallize the synthesized silicon carbide; alternatively the milling parameters were not optimized enough hence a "poorer" sample was subjected to the firing. However a temperature much greater than 900 °C would not be advantageous in the context of nuclear waste processing, the results are encouraging in that only longer dwell period may be sufficient in obtaining a better product (given that the other parameters are sufficiently optimized). The investigation into higher temperature sintering of the same sample may be sound basis for future work (for the ease of further characterization of the synthesis product). This may result in a higher rate of crystallization for not only unreacted precursors such as the silicon and carbon but potential amorphous silicon carbide (if present).

XRD was a useful technique in the scope of this project, however there were some drawbacks primarily associated with its reliance on crystalline phases to be present. In the case where the samples were recrystallized sufficiently, the technique would have been far more useful providing information about the structure of the synthesis product. In addition, it was noted that the XRD did not detect any materials other than silicon, carbon and silicon carbide, hence confirming that the sample was not contaminated during the processing.

SEM analysis was conducted on unfired samples to examine the microstructure of the samples. It was found that all samples exhibited high levels of agglomeration as seen in Figure 3a, this was common for all samples #1-3. From

visual inspection of images of samples milled for 2 and 10 hours it was noted that the average size of the agglomeration reduces with milling period and the packing density of the particles within the agglomerations increases as well. From this, it may be inferred that the particle size distribution increases in the initial phase of the milling. A higher packing density of the particles is an advantage when considering the re-use of the wastefrom in the reinforcement of cements and disposal, as it reduces the wastefrom volume, however the effects or their scale of the higher packing density of the silicon carbide on the mechanical properties of the cement is unknown.

As a result of difficulty in assessing the particle size of the constituent particles of the agglomerates, subsequent samples were subject to sonication during sample preparation whereby the agglomerations, some of which were up to 40 μm in size, were broken down to less agglomerated particles in isopropyl alcohol solution. It must be noted that the agglomerations were of a large size distribution. This solution was then taken and appropriate amounts left on sample holders, where the alcohol solution evaporated over time to leave a film of the sample upon the adhesive carbon tape of the sample holder.

Subsequent imaging of the sonicated samples showed far less signs of agglomeration, however there were certain effects as a result of the sonication process. As seen on figure 3b, the sample is remarkable different in terms of its shape and arrangement as a direct result of the processing, it is no longer made up of many large agglomerations, but instead is a continuous film made up of the particles. For samples #1-3 it was seen that there was some unquantifiable change in the samples, however it is not possible to say whether this is due to the sonication process or the different samples. However at much higher resolution it was clear that all the samples had very similar levels of agglomeration and similar microstructure. Higher magnification would have provided a good estimation of the average particle size, however microscope limitations and problems prevented this.

EDS was carried on multiple samples, and the same signature trace as in Figure 3d was obtained, note that on Figure 3c the point at which the EDS was performed is marked. The EDS traces all exhibited the same signature shape, which featured a major silicon peak but generally only a dwarfed carbon peak. Literature indicates that this is expectable as the sensitivity of the EDS to lighter elements such as carbon is low. As this technique is only elemental, it could not detect the presence of silicon carbide, however it did detect that there was little or no contamination from the milling process to the sample. EDS was repeated for several particles in each sample, including very small particles, particles isolated from other particles and large agglomerates; all produced very similar traces.

DTA was conducted to determine the presence of silicon carbide, sample #1 post milling but without additional sintering stage, with sintering at 600 $^{\circ}\text{C}$ and with sintering at 900 $^{\circ}\text{C}$, were all analyzed. The traces, shown in Figure 4a-c, all had the same signature shape, which is expected as the precursors are the same. However the striking difference is that the large exothermic peak, which dominates the trace, changes. The peak is due to the oxidation of the carbon [25], within the sample, where the area beneath this peak is proportional to the amount of energy liberated during the oxidation of carbon. Hence the quantity of free carbon is diminishing with the firing process and even more as the firing temperature is increased. This is encouraging as an explanation is that with firing the rate of silicon carbide is higher more so as the firing temperature increases, more carbon is utilized in the synthesis of silicon carbide.

In addition to this peak, a very small peak is also of great significance between 1050 and 1080 $^{\circ}\text{C}$, which may refer to one of a number of different processes, however the most likely seems to be the oxidation of silicon, which occurs between 800 and 1200 $^{\circ}\text{C}$. In the presence of silicon carbide, the silica layer forms on the surface of the silicon carbide at temperatures of approximately 1050 $^{\circ}\text{C}$ [26]. This is a well known process as the passive silica layer is what gives silicon carbide its high oxidation resistance. It is clear also that the trace indicates that there are no exothermic processes until 500 $^{\circ}\text{C}$, which is advantageous when considering its application as a wastefrom, especially if considering the insertion of the synthesis product into cements, which generate heat upon setting.

The experiment considers graphite powder as a suitable precursor, however accuracy with which this mimics the radioactive graphite obtained from decommissioned nuclear reactors is unclear, yet this project provides a brief

insight into some of the challenges faced when optimizing this low temperature mechanochemical alloying synthesis route for the immobilization of silicon carbide.

An experimental limitations which could not be avoided, was the absence of regular milling profiles. Limited access to the mill resulted in erratic milling profiles, the full effect of which is unknown. However what is clear is that heat generation from the milling is lower during shorter milling periods and this may affect the work-hardening, fracturing and rewelding mechanism of the mechanical alloying. In addition a more effective milling profile will result in a better sample ready for firing, hence fired samples are expected to be more crystalline and have a lower carbon content. The process, albeit requiring optimization, is promising in the application of irradiated graphite immobilization.

CONCLUSIONS

The results obtained are encouraging and strongly suggest that silicon carbide has been synthesized, although the yield is likely to be low yet. This however does indicate that this specific processing route has great potential in realizing the aims set out in the introduction of this paper, that is to immobilize irradiated waste graphite at relatively low temperatures via a two stage mechanochemical synthesis technique followed by incorporation of silicon carbide into a final either ceramic or cementitious wasteform or barrier material.

SEM analysis shows a deal of agglomeration, where the size of the agglomerates and packing density of the particles in the agglomerations decreases and increases respectively with increased milling periods. XRD analysis indicates the presence of silicon carbide and that with increased milling periods significant amorphisation of the precursors occurs. The ratio of silicon to graphite powders in the samples had very little effect on the final samples, regardless of whether additional firing stages were carried out, however this may be due to ineffective milling and small sample sizes.

DTA analysis showed that samples, which had been milled and not fired, did not differ significantly, when the firing stage was conducted at 600 °C. However in comparison with samples milled and fired at 900 °C significant change was apparent.

Although this preliminary investigation into the viability of mechanochemical processing technique was successful and agrees with data obtained by others [19], further work is to be conducted into the optimization of the process such that the synthesis product and the process itself is better understood. The optimization of parameters such as milling period, milling profiles, and firing parameters will be considered.

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